



Harniman, R., Plana, D., Carter, G., Bradley, K., Miles, M., & Fermin, D. (2017). Real-Time Tracking of Metal Nucleation via Local Perturbation of Hydration Layers. *Nature Communications*, 8, [971]. <https://doi.org/10.1038/s41467-017-01087-1>

Publisher's PDF, also known as Version of record

License (if available):
CC BY

Link to published version (if available):
[10.1038/s41467-017-01087-1](https://doi.org/10.1038/s41467-017-01087-1)

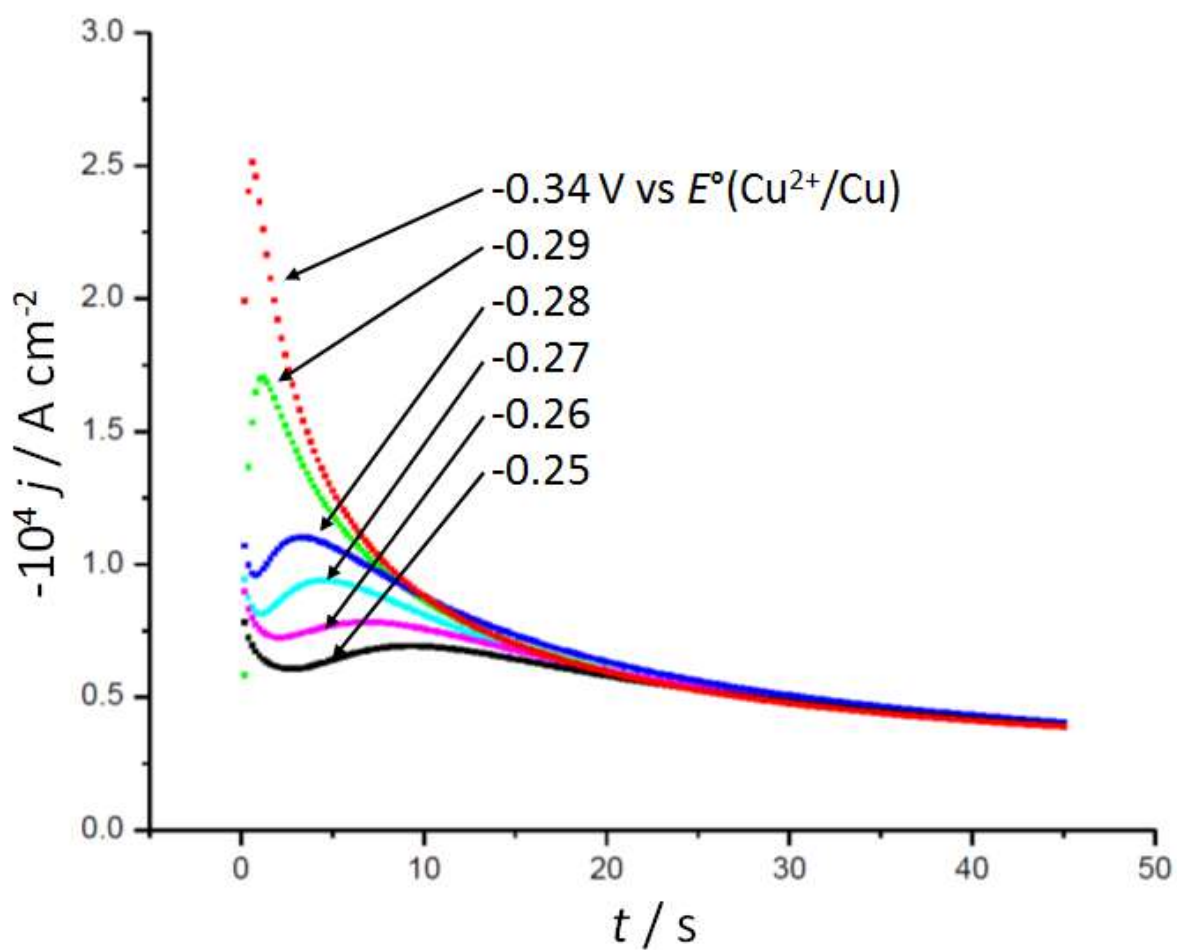
[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the final published version of the article (version of record). It first appeared online via Nature at <https://www.nature.com/articles/s41467-017-01087-1>. Please refer to any applicable terms of use of the publisher.

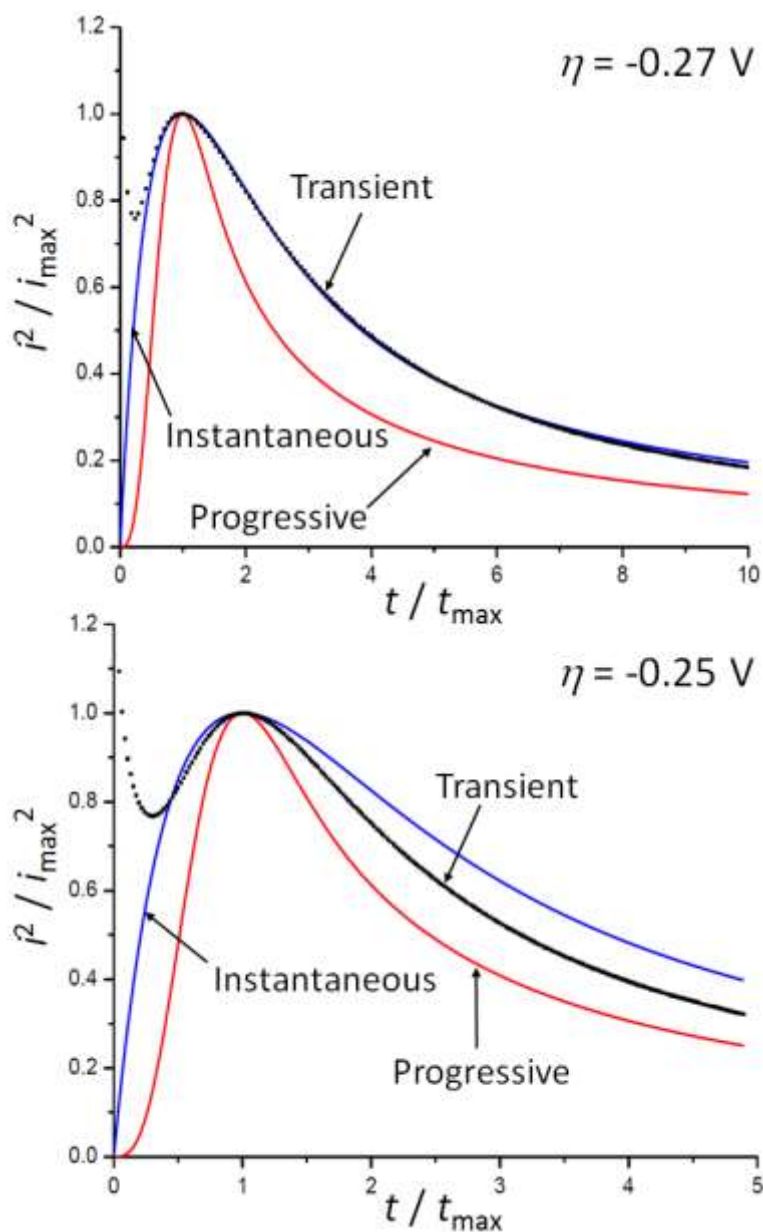
University of Bristol - Explore Bristol Research

General rights

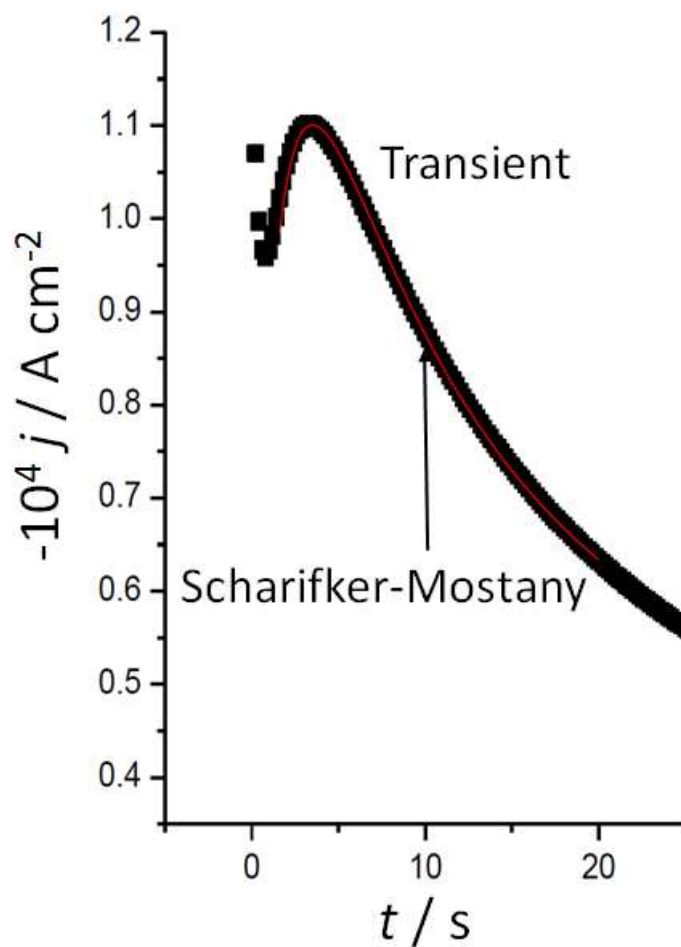
This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available: <http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>



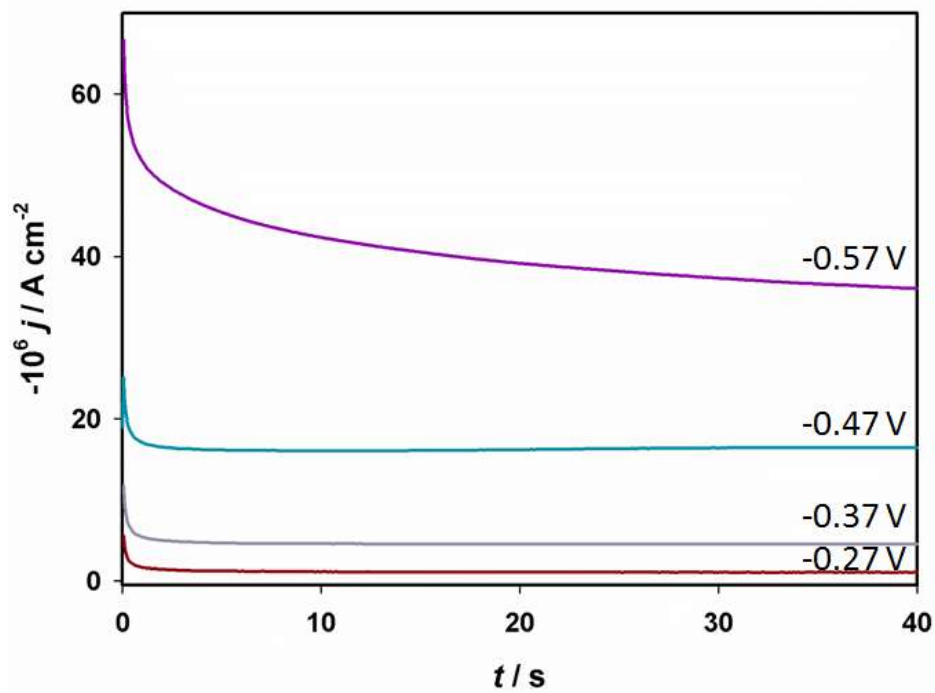
Supplementary Figure 1. Characteristic chronoamperometric transients at ITO electrodes in aqueous solution of CuSO_4 $1.0 \times 10^{-3} \text{ mol} \times \text{dm}^{-3}$ at various overpotentials and room temperature. The electrolyte solution contained $50 \times 10^{-3} \text{ mol} \times \text{dm}^{-3}$ Na_2SO_4 at pH 3.



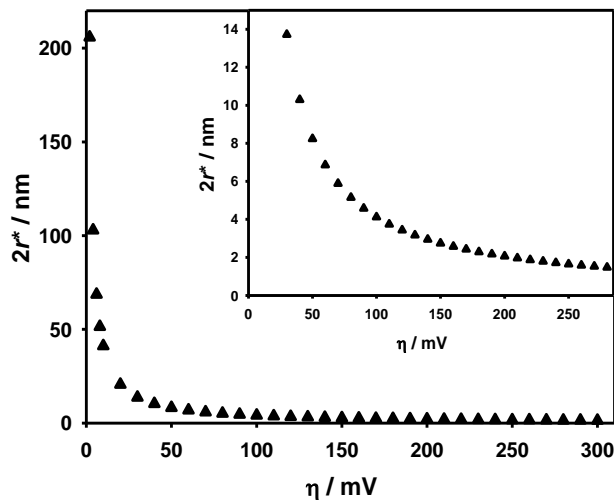
Supplementary Figure 2. Dimensionless plot of the current (i) normalised by the maximum current (i_{\max}) as a function of time (t) at two overpotentials. The experimental conditions are described in the caption of **Supplementary Figure 1**. The *instantaneous* and *progressive* nucleation limits as predicted by the Scharifker-Hills model¹ are indicated.



Supplementary Figure 3. Chronoamperometric transient recorded at -0.27 V fitted to the Scharifker-Mostany model.² Concentration of CuSO_4 is $1.0 \times 10^{-3} \text{ mol} \times \text{dm}^{-3}$. Nuclei number density and nucleation rate of $5.3 \times 10^6 \text{ cm}^{-2}$ and 15 s^{-1} , respectively, were estimated from the fit.



Supplementary Figure 4. Chronoamperometric transients recorded at various overpotentials on ITO electrodes at a CuSO_4 concentration of $1.0 \times 10^{-4} \text{ mol} \times \text{dm}^{-3}$. Other experimental conditions are described in the caption of **Supplementary Figure 1**. The lack of a well-defined current peak and diffusion limiting current suggest a convolution of the dynamics of electron transfer and nucleation.



Supplementary Figure 5. Critical nucleus diameter ($2r^*$) as a function of the overpotential (η), estimated from **equation 1**. In **equation (1)** σ represents the surface tension, M is the atomic weight (M) and ρ is the density.³ This simple relation predicts stable Cu nuclei of 1.5 nm diameter can be formed at overpotentials of -0.27 V. Our experimental observations based on HS-LMFM images revealed stable nuclei of the order of 6-7 nm. Considering that no tip-shape deconvolution routines were applied to these images, our experimental values are close to the thermodynamic limit.

$$r^* = 2\sigma M / \rho z F |\eta| \quad (1)$$

Supplementary References

- 1 Scharifker, B. & Hills, G. Theoretical and Experimental Studies of Multiple Nucleation. *Electrochim Acta* **28**, 879-889 (1983).
- 2 Scharifker, B. R. & Mostany, J. 3-Dimensional Nucleation with Diffusion Controlled Growth.1. Number Density of Active-Sites and Nucleation Rates per Site. *J Electroanal Chem* **177**, 13-23 (1984).
- 3 Scharifker, B. R. & Mostany, J. in *Encyclopedia of Electrochemistry: Interfacial Kinetics and Mass Transport* Vol. 2 (eds A.J. Bard, M. Stratmann, & E.J. Calvo) 512-540 (Wiley, 2003).